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**Title:** A Complete EOS Formulation for Prescribing a Fluid of Reacting Products An analytical formulation of a deformable sphere classical partition function for describing a continuous fluid of idealized particles that follow effective inter-particle potential energy

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# A Complete EOS Formulation for Prescribing a Fluid of Reacting Products

An analytical formulation of a deformable sphere  
classical partition function for describing a continuous  
fluid of idealized particles that follow effective  
inter-particle potential energy

Jonathan Lee Mace <sup>1</sup>   Travis B. Peery <sup>2</sup>

Tri-Lab Dialogue on Weapon Response

December 4–8, 2017

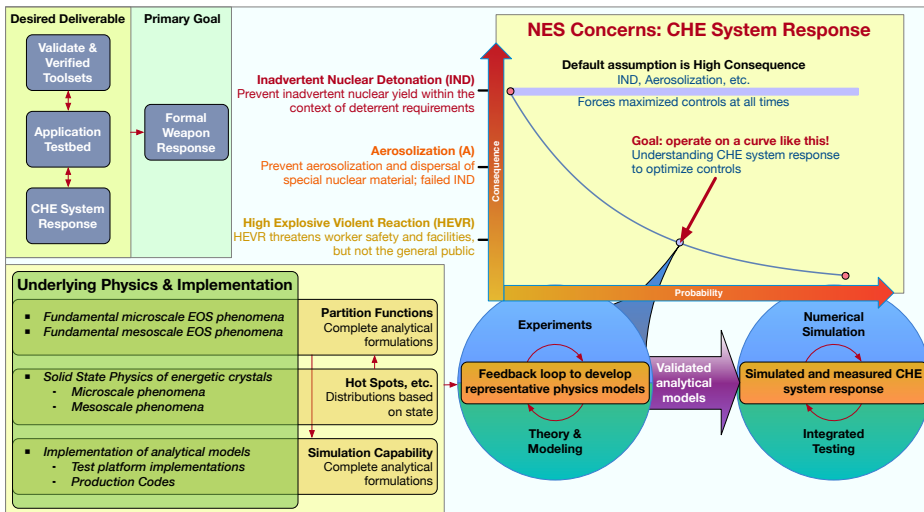


## Section 1

A new program intended to address the response of  
dynamically damaged CHE systems

# **CHE System Grand Challenge (CHESGC): Preliminary Results and Ideas**

# Summary: How does this EOS formulation fit into the CHESGC Program?



## Section 2

**A classical continuous field of material elements is assumed, and a classical partition function is analytically solved in the Helmholtz free energy representation**

### **A Brief Outline of Key Ideas Central to the Development of a Complete Deformable Sphere EOS Formulation**

## Subsection 1

### **An assumed continuum hypothesis** **Continuous Classical Field Assumptions**

# Mass, momentum and energy conservation

1. A fluid of interacting idealized particles is **assumed**.
2. Differential system  $\mathcal{D} = \{\mathcal{L}[\psi_i]\}$ , composed of continuity eqns

$$\mathcal{L}[\psi_i] = \frac{\partial \psi_i}{\partial t} + \nabla \cdot \mathbf{J}_{\psi_i} = 0, \quad \psi_i \in \{\rho, \rho v_1, \rho v_2, \rho v_3, \rho E\},$$

$$0 = \mathcal{L}[\psi_i^{(1)} + \psi_i^{(2)}],$$

is not a closed system (more unknowns than equations).

3.  $\mathcal{D}$  is closed by **assuming** a set of normalized EOS relations  $\mathcal{E}_\mu$ :

$$\mathcal{E}_\mu = \begin{cases} X_i \in \{u, v, n\} & \text{extensive state variables} \\ s(u, v, n) & \text{entropy} \\ Y_1 = t(u, v, n) & \text{temperature} \\ Y_2 = p(u, v, n) & \text{pressure} \\ Y_3 = m(u, v, n) & \text{chemical potential} \end{cases}$$



# Thermodynamic limit + Classical continuous field

## 1. The thermodynamic limit

$$f = \lim_{N \rightarrow \infty} \frac{F}{N}, \quad F = -k_B T \ln Z_N(T, V) \text{ is Helmholtz free energy,}$$

is **assumed** to remain finite, well behaved, and physically relevant.

## 2. Assume a continuous field of differential material elements,

$$\mathbf{a}(\mathcal{E}_\mu) = a_1(\mathcal{E}_\mu) \hat{a}_1 + a_2(\mathcal{E}_\mu) \hat{a}_2 + a_3(\mathcal{E}_\mu) \hat{a}_3 \text{ with initial state } \mathbf{a}(\mathcal{E}_\mu^{(0)}),$$

and note that conservation relations encapsulated within  $\mathcal{D}$  are now based entirely on  $\mathcal{E}_\mu$ , thermodynamic derivatives within  $\mathcal{E}_\mu$ , and derivatives  $\partial^m X_i / \partial a_j^n \partial a_k^p \dots$ ,  $m = n + p + \dots$ .

### 2.1 Put succinctly, $\mathcal{D}$ is **assumed** to dictate the conservative **quasi-static** evolution of material elements over entropy surface $s(u, v, n)$ .

# Assume a continuous, well defined mapping between thermodynamic & material coordinates

## 1. Thermodynamic coordinates:

$$\mathbf{X}(\mathbf{a}) = X_1(\mathbf{a}) \hat{X}_1 + X_2(\mathbf{a}) \hat{X}_2 + X_3(\mathbf{a}) \hat{X}_3$$
$$\nabla_{\mathbf{X}} = \frac{\partial}{\partial X_1} \hat{X}_1 + \frac{\partial}{\partial X_2} \hat{X}_2 + \frac{\partial}{\partial X_3} \hat{X}_3$$

## 2. Material coordinates:

$$\mathbf{a}(\mathbf{X}) = a_1(\mathbf{X}) \hat{a}_1 + a_2(\mathbf{X}) \hat{a}_2 + a_3(\mathbf{X}) \hat{a}_3$$
$$\nabla_{\mathbf{a}} = \frac{\partial}{\partial a_1} \hat{a}_1 + \frac{\partial}{\partial a_2} \hat{a}_2 + \frac{\partial}{\partial a_3} \hat{a}_3$$

3. **Note:** Many or all of material elements  $\{\mathbf{a}\}$  can exist at a single point  $\mathbf{X}$  on surface  $s(\mathbf{X})$ , so the mapping from  $\{\mathbf{a}\}$  onto  $s(\mathbf{X})$  is not generally one-to-one (injective).

# Assumed local equilibrium hypothesis

1. Mathematically a continuous classical field of differential elements is **assumed**, the physical state of each element is defined by a specific point  $\mathcal{E}_\mu$  in EOS space, and changes in  $\mathcal{E}_\mu$  associated with any particular element occur in a quasi-static manner over  $s$ .
2. This is accomplished by envisioning a material element of density  $\rho = m\delta N/\delta V$ , occupying an initial thermodynamic volume  $\delta V = \delta a_1\delta a_2\delta a_3$  and composed of  $\delta N$  particles, with  $\delta N$  sufficiently large such that the statistical significance required to define  $Z_N(T, V)$  is achieved, and, simultaneously, with  $\delta V$  sufficiently small such that it approximates a differential material element, and then by **assuming**

$$\lim_{\substack{\delta N \rightarrow 0 \\ \delta V \rightarrow 0 \\ \frac{\delta N}{\delta V} = \frac{\rho}{m}}} a(\mathcal{E}_\mu) = a(\mathcal{E}_\mu),$$

where  $m$  is constant particle mass.

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where  $m$  is constant particle mass.

## Local equilibrium hypothesis (continued)

3. This limit enables standard calculus across the continuous field of differential elements, and, when combined with a specific EOS in the thermodynamic limit, is referred to **here** as the **local equilibrium hypothesis**.
4. In this limit nearest neighbor elements remain nearest neighbor elements throughout the evolution of the field, provided that the **assumption** of continuity remains valid.
  - 4.1 Continuity is **assumed** throughout this theory, and therefore surface boundaries along which material elements slip past one another cannot develop within bulk material.
  - 4.2 It is **assumed** that all processes considered within the CHESGC are approximately quasi-static over EOS surface  $\sigma$ ,  
(electronic and nuclei vibrational timescales)  $\ll$   $\tau_{\text{CHESGC}}$   
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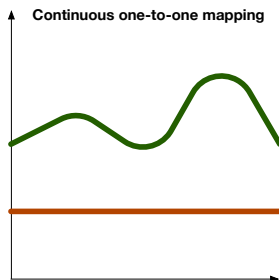
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# Reminder about continuous mappings



**Figure:** A continuous one-to-one mapping exists between the red and green lines. Similarly there is a continuous one-to-one mapping as the continuous field of differential elements moves and distorts. Constant volume shear, for example, is not considered within the context of this assumed local equilibrium hypothesis since nearest neighbors cannot slip past one another, nor is it necessary for the physics that  $\mathcal{E}_\mu$  is intended to approximate.

## Subsection 2

**Deformable idealized particles that follow effective  
inter-particle potential energy  
Development of a Complete set of EOS relations**

# Formulation and application of EOS $\mathcal{E}_\mu$

## 1. Analytical formulation of $\mathcal{E}_\mu$ from the classical partition function:

1.1  $Z_N(T, V) = Z_0(T, V) \mathcal{P}_N^{(i)}$  where  $\mathcal{P}_N^{(i)} \xrightarrow{V_{ij} \rightarrow 0} \frac{V^N}{V^N} = 1$ :

{100s randomly oriented intermediary species +

many shapes and sizes}  $\xrightarrow[n_i \gg 1, i \in \{1, \dots, n\}]{\text{number states} \sim N_i!}$  effective

{spherical symmetry + non-relativistic idealized deformable particles +  
inter-particle potential energy per molecular dynamics (MD)}

1.2 Effective center of mass excluded volume (CMEV) is formulated, each such contribution to  $\mathcal{P}_N^{(i)}$  is appropriately weighted by an effective inter-particle potential energy Boltzmann factor, and all cluster sizes are counted up to a maximum size in correspondence to system density.

1.3 Fluctuation theory is utilized to calculate an average partition function in correspondence to system density, resulting in a complete set of smoothly varying effective thermodynamic functionalities (underway).

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# Formulation and application of EOS $\mathcal{E}_\mu$ (continued)

2. A complete set of EOS relations derive from the classical partition function  $Z_N(T, V)$ , and are denoted by  $\mathcal{E}_\mu$ .
  - 2.1 Reaction rate and ignition criteria are not required since idealized particles do not combine or separate in accordance with stoichiometric requirements, but instead follow effective inter-particle potential energy  $V_{ij}$  as a function of average inter-particle separation. **Reaction is implicit in the model.**
  - 2.2 Solid state physics and mesoscale effects are addressed in separate theories. One primary goal is to marry  $\mathcal{E}_\mu$  with these theories as they evolve.
  - 2.3 The set of relations  $\mathcal{E}_\mu$  is utilized to develop relevant transport relations within the fluid without reference to spacetime coordinates; e.g., the conduction of  $u$ ,  $n$  between elements, bulk and shear viscosities, etc.
3. Progresses made in formulating  $\mathcal{E}_\mu$  are not summarized here.
4. A strategy for constructing high-order applications of  $\mathcal{E}_\mu$  is currently being developed.

## Some important notes...

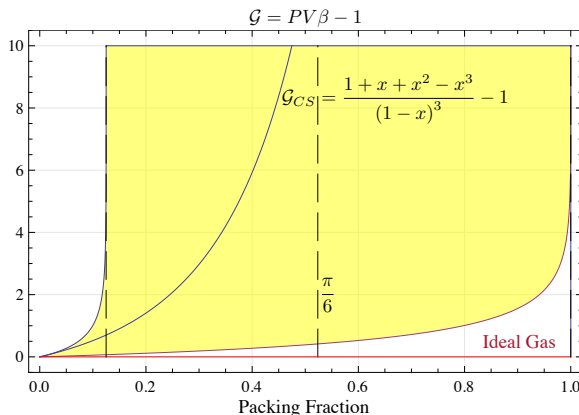
1. Fluid of interacting idealized deformable particles:
  - 1.1  $\langle \text{chemical effects} \rangle$  are approximated within  $Z_N(T, V)$  via  $V_{ij}$  as potential energy Boltzmann factors that appropriately weight each interaction counted in configuration integral  $\mathcal{P}_N^{(i)}$ .
  - 1.2 100s intermediaries, 1000s reaction pathways  $\xrightarrow[\text{simulations}]{\text{MD}}$   $V_{ij}$
  - 1.3 Since reaction progress is explicitly tracked in MD simulations, only the resulting average effective inter-particle energy need be incorporated into  $Z_N(T, V)$ ; i.e., a reaction progress coordinate is not explicitly required, but instead  $V_{ij}$  Boltzmann factors are incorporated as a function of inter-particle separation parameter  $s$ .
2. CMEV effects are approximated for all cluster sizes and densities, and are crucial in a useful approximation to  $\mathcal{P}_N^{(i)}$ .
  - 2.1 Idealized deformable particles are assumed to statistically represent a random “soup” composed of hundreds of intermediary species.
  - 2.2 To our knowledge the CMEV problem has not been solved before.



## Subsection 3

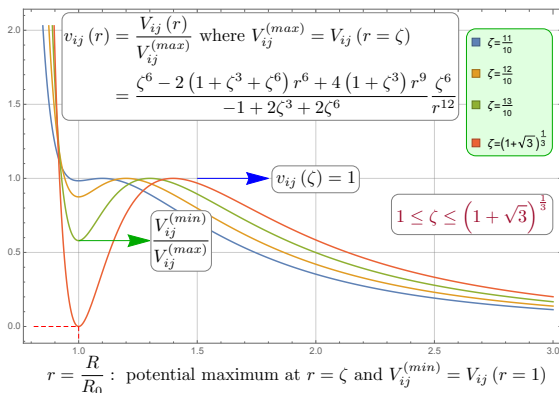
**A brief sketch of some of the thinking and results**  
**Overview of the Partition Function Development**

# Visualization of effective packing fraction



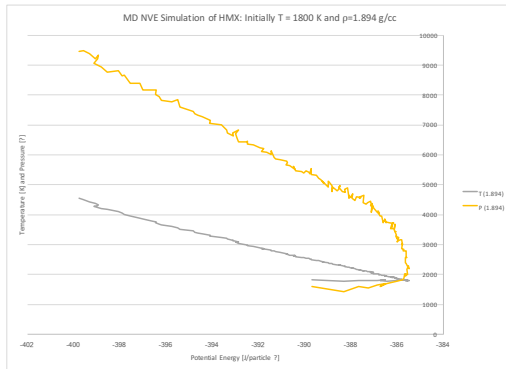
**Figure:** Deviation from the ideal gas as a function of packing fraction. The work done by an HE predominately occurs at packing fractions  $\mathcal{F}_\Gamma < \mathcal{F}$ , where the packing fraction of effective idealized particles can exceed 1.

# Effective inter-particle potential energy $V_{ij}(s)$ (example)



**Figure:** A Lennard–Jones 6–12 potential plus a  $1/r^3$  dipole repulsion is assumed for illustrative purposes. Ultimately this expression will be replaced by an effective inter-particle potential energy surface, derived from MD simulations for each specific HE formulation (Ed Kober).

# PBX 9501 $V_{ij}(s)$ from MD constant $(N, V, E)$ simulations



**Figure:** Example MD Simulation of HMX with initial conditions  $T = 1800$  K and  $\rho = 1.894$  g/cc. A smooth fit to this data and a conversion algorithm to our model must be constructed, and then the result must be smoothly “stitched” into the assumed  $[\text{LJ } 6-12] + [1/r^3 \text{ dipole repulsion}]$  model.

# Construction of $Z_N(T, V) = Z_0(T, V) \mathcal{P}_N^{(n)}$

Configuration integral  $\mathcal{P}_N^{(n)}$  specifies the deviation from an ideal gas due to CMEV interactions. Each such interaction is appropriately weighted by an  $V_{ij}(s)$ -based Boltzmann factor. Complex continuous interactions  $\rightarrow$  digital effective interactions.

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} \sum_{\substack{i,j=1 \\ j \neq i}}^N V_{ij}(x_{ij}) \rightarrow$$

$$Z_N(T, V) = \frac{1}{C^N} \int_{\Gamma} e^{-\beta H(\chi^N)} d\chi^N, \quad c^N = h^{3N} \begin{cases} d_p = N! & \text{indist.} \\ d_p = 1 & \text{dist.} \end{cases}$$

$$\xrightarrow{\text{ASM 4.3}} Z_0(T, V) \mathcal{P}_N^{(n)}, \quad V_{\Gamma}|_{\text{continuous}} \gg V_{\Gamma}|_{\text{digital}}$$

$$\xrightarrow{\text{ASM 3, 4.4}} \mathcal{P}_N^{(n)} = \prod_{i=1}^n (\mathcal{R}_{N_i})^i \mathcal{B}_{N_i} \text{ is determined analytically, where}$$

$$\mathcal{P}_N^{(i)}(T, V) = \frac{1}{V^N} \int_{V_1} \cdots \int_{V_N} e^{-\frac{\beta}{2} \sum_{j=2}^N V_{1j}} \cdots e^{-\frac{\beta}{2} \sum_{j=1}^{N-1} V_{Nj}} d^3 x_1 \cdots d^3 x_N$$

# $\mathcal{R}_{N_i}(x_i)$ in the limit $N_\infty$ and $\mathcal{B}_{N_i}^{(i)}$ and $Z_N(T, V)$

$$\mathcal{R}_{N_i}(x_i) = \frac{P_{N_i}^{(i)}(x_i)}{P_{N_{i-1}}^{(i)}(x_i)} \text{ where } x_i = \frac{g_i(s)\Omega_0}{V} \text{ and } \frac{d \ln x_i}{dV} = \frac{d \ln g_i}{ds} \frac{ds}{dV} - \frac{1}{V}$$

$$\ln \mathcal{R}_{N_i}(x_i) = \frac{N_i}{i} \delta \left( \frac{N_i x_i}{i} \right) - \frac{N_{i-1}}{i} \delta \left( \frac{N_{i-1} x_i}{i} \right)$$

$$\frac{\partial \ln \mathcal{R}_{N_i}(x_i)}{\partial x_i} = \left( \frac{N_i}{i} \right)^2 \delta' \left( \frac{N_i x_i}{i} \right) - \left( \frac{N_{i-1}}{i} \right)^2 \delta' \left( \frac{N_{i-1} x_i}{i} \right)$$

$$\frac{\partial \ln \mathcal{R}_{N_i}(x_i)}{\partial N_i} = \ln \left( 1 - \frac{N_i x_i}{i} \right)$$

$$\frac{\partial \ln \mathcal{R}_{N_i}(x_i)}{\partial V} = \frac{1}{x_i} \frac{d \ln x_i}{dV} \left[ \frac{N_i x_i}{i} - \frac{N_{i-1} x_i}{i} + \ln \frac{1 - \frac{N_i x_i}{i}}{1 - \frac{N_{i-1} x_i}{i}} \right]$$

$$\mathcal{B}_{N_i}^{(i)} = \exp \left[ -\frac{c\tilde{\beta}}{2} ((N_i - 1) v_{ij}(s_k) - (N_{i-1} - 1) v_{ij}(s_{i-1})) \right], s_k = \begin{cases} s_i & s_i > s \\ s & s_{i-1} > s \geq s_i \end{cases}$$

Partition function corresponding to a single maximum cluster size:

$$Z_N(T, V) = Z_0(T, V) \prod_{i=1}^n \left[ \mathcal{R}_{N_i} \left( \frac{g_i(s_k)\Omega_0}{V} \right) \right]^i \mathcal{B}_{N_i}^{(i)}(s_k), s_k = \begin{cases} s_i & i < n \\ s & s_{n-1} > s \geq s_n \\ & \text{when } i=n \end{cases}$$

# Helmholtz free energy: $F = -k_B T \ln Z_N(T, V)$

Helmholtz free energy per particle for a single maximum cluster size:

$$f = \frac{F}{N} = f_0 - k_B T \sum_{i=1}^n \left\{ \tilde{N}_i(s_k) \delta \left( \frac{N_i(s_k) x_i(s_k)}{i} \right) - \tilde{N}_{i-1} \delta \left( \frac{N_{i-1} x_i(s_k)}{i} \right) - \frac{c\tilde{\beta}}{2} \left[ \tilde{N}_i(s_k) v_{ij}(s_k) - \tilde{N}_{i-1} v_{ij}(s_{i-1}) \right] \right\}$$

$$s = -\frac{\partial f}{\partial T} = \frac{3}{2} k_B - \frac{f}{T} - k_B \frac{c\tilde{\beta}}{2} \sum_{i=1}^n \left[ \tilde{N}_i(s_k) v_{ij}(s_k) - \tilde{N}_{i-1} v_{ij}(s_{i-1}) \right]$$

$$u = f + Ts = \frac{3}{2} k_B T - k_B T \frac{c\tilde{\beta}}{2} \sum_{i=1}^n \left[ \tilde{N}_i(s_k) v_{ij}(s_k) - \tilde{N}_{i-1} v_{ij}(s_{i-1}) \right]$$

## $F(T, V, N)$ and $U(S, V, N)$ representations and volume:

1.  $F(T, V, N)$  representation:  $S = S(T, V, N)$ ,  $P = P(T, V, N)$ ,  $\mu = \mu(T, V, N)$
2.  $U(S, V, N)$  representation:  $T = T(S, V, N)$ ,  $P = P(S, V, N)$ ,  $\mu = \mu(S, V, N)$
3. Volume is  $V = V(s)$  where  $s$  is inter-particle separation parameter, not entropy

## Acknowledgements:

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# Questions?